

The results of the fourth edition of the LBMA gold (>995‰) proficiency testing have been released. This paper, presented at the LBMA 2015 Assaying and Refining Conference in London on 9 March, details how samples are prepared, what results were obtained and what can be learned from the exercise.

I. Introduction

In the precious metal industry, laboratory staff are extremely important people. If they don’t do their job properly, there is a huge risk for the company, which can take the form of lost metal, compliance problems or reputation issues. There are many tools allowing laboratories – and management – to control the quality of analyses performed, and one of those is proficiency testing (also called round robin). In 2012, the LBMA launched its own annual Proficiency Testing (PT) scheme, and the results of the fourth scheme were released just a couple of weeks ago.

Why join a Proficiency Testing scheme?

There are many reasons to join a proficiency testing scheme (see chart 1). For laboratories, the most frequently cited reason is that such participation is a requirement of ISO 17025, as this accreditation requires all laboratories to perform inter-laboratory testing on their accredited methods.

There are, however, other attractive reasons.

- Issues on analyses can potentially be detected. While most laboratories believe they provide the best analyses in the market, it is not always the case. Pinpointing specific problems can be complex; proficiency testing can provide such information, especially when a scheme is joined for several years in a row.
- Assessment of the performance and capability of the analytical staff can be performed. This is crucial not only for the lab manager, but for the management of the company; both enjoy the assurance that the analytical job is performed properly. A PT organised by a third-party organisation is usually trustful.
- Comparison of a laboratory’s performance with a large number of competitors can be done only through participation in such a scheme.
- Validation of new analytical methods is often complex. Over the last four years, we have seen many laboratories starting to rely heavily on spectroscopic methods, while fire assay was the reference method in 2012. It is likely that some spectroscopic methods were validated in-house with the use of the LBMA PT.
- Equipment change and training can be justified. Obtaining budget for buying a new ICP-OES is not always easy nowadays, but PT results can help justify such an investment.

II. Sample Composition and Preparation

The LBMA wants to ensure that a significant variety of compositions is proposed for the proficiency testings, covering purity of between 995 and 999.9‰, and corresponding to ‘real-life’ materials. This means that binary samples containing only gold and silver as an impurity are not attractive, and nor are materials with exotic elements. The idea is rather to have samples that could correspond to what is obtained at a refinery. Importantly, all samples are specifically prepared for the proficiency testing, which is a requirement to get an appropriate homogeneity.

The procedure starts with the LBMA and the referees deciding on a specific composition (see chart 2). One referee will prepare the samples, analyse them and provide data on homogeneity to the LBMA. In parallel, a second referee will...
independently test the homogeneity. This double verification is very important: samples that are not rigorously homogeneous would be of no use for the scheme. Samples are then sent to FAPAS, which in turn sends the samples to the laboratories. Once the samples have been analysed, the results are sent back to FAPAS, which will anonymise them and forward them to the LBMA and the referees.

Again, note that neither the LBMA nor the referees know which result was provided by any given company, so the PT is really a tool to control each laboratory’s own ability. While the LBMA cannot monitor each refiner’s performance, PT gives information on how the market is doing and indicates, sometimes, that the results are not as precise as we all would like them to be.

Chart 3 shows the composition of the four samples analysed between 2012 and 2015, with the bars representing the amount of impurities (in ppm, part per million). In 2012, we had a 995.4‰ sample, with mostly silver and some copper as impurities. The following year, the sample contained fewer impurities. In 2014, we focused on a slightly unusual 997‰ sample with more copper than silver – something we have seen more and more in the market. And this year, we had a sample with a very low impurity level, above 999.5‰. Apart from the main elements – silver, platinum, palladium and copper – we have always had a couple of extra elements, and the list is open to change in the future.

The central data obtained from any proficiency testing is the Z-score (should you remember only one piece of information for your result, it should be that number). It is defined from two factors: the target value, which is the average of all valid results given by laboratories; and the acceptable standard deviation, fixed at 0.049‰. This value was calculated from assays performed for the LBMA over 10 years and fixes the precision we want to achieve. Since the target value is an average of averages, rather than a number defined by the referees, the PT scheme is valid only if you have a large number of laboratories participating, typically more than 30.

- Laboratories want to achieve a Z-score of between -2 and 2: 85-95% of laboratories reached that important goal.
- A Z-score of between 2 and 3 (and between -2 and -3) is a little tricky. It means that it is not possible to say whether the laboratory has a bias or not: the result is borderline.
- Laboratories within those zones should consider the result as a warning and carefully check whether there is a potential problem. Most importantly, they should join the next proficiency testing either to corroborate this bias or to confirm that there was no error.
- Z-scores above 3 and below -3 are seriously concerning and mean that from the statistical point of view, the laboratory is outside the range it should be in. Until last year, we always had one lab outside the range; this year, we had two.

Spectroscopic methods that we have not seen yet are MP-AES, using a plasma generated by a microwave, and ICP-MS, whose usage has been developed by several companies but to the best of our knowledge has never been applied to qualify high-purity gold at PT.

The use of SPARK-OES was both surprising and exciting. SPARK ablation is a fantastic technique, because it is extremely stable.

The main difference between spectroscopic analysis and fire assay is their respective precision, while accuracy is usually similar (see chart 4). The results from 2012-15 are normalised to 1,000 (the target value). All values are very close to 1,000, with no significant difference between ICP-OES and fire assay (the 2012 ICP-OES result is biased by the very small number of labs using that instrument).
Spectroscopic analysis is extremely powerful when samples contain a low amount of impurities. In 2014, with 3,000 ppm of impurities, the precisions of ICP-OES and fire assay were more or less identical. However, when we go to material with a higher purity, we see a significant difference between fire assay and spectroscopic analysis, with ICP-OES being much more precise.

Interestingly, we do not observe a significant variation between accredited and non-accredited laboratories using fire assay.

ICP-OES is an extremely powerful method for the determination of each specific impurity. In 2014, we measured a little over 1,000 ppm for silver, with a standard deviation of 39 ppm (4%). For copper, the standard deviation was about 5%. In 2015, the results were also interesting, with every single impurity – silver at about 2,000 ppm, and platinum, palladium and zinc at about 10 ppm – having a standard deviation of about 10%.

VI. 2015 Results

Chart 5 shows all the results from accredited and non-accredited laboratories, as well as the LBMA accepted deviation (as illustrated by the red lines). During an application, 999.5‰ gold has to be provided to the LBMA with an accuracy of 50 ppm, which means that every result above or below this level would have been classified as a failure. Two labs not on the Good Delivery List announced a far too high purity for the sample (above 999.8‰). At the same time, other accredited laboratories delivered results that were extremely far from the expected value. Any laboratory with an abnormal result really needs to take action and to seek advice to fix the issue.

Any laboratory with an abnormal result really needs to take action and to seek advice to fix the issue.

A recurrent problem with this is that laboratories tend to overestimate the precision of their method. For each lab, the standard deviation is represented by vertical lines which should cross the target value. This however is not the case for most laboratories. A possible reason could be that the highest and lowest replicas are removed from the list of results, which often does not change the average, but does seriously diminish the uncertainty and gives a false sense of safety.

VII. Conclusion

It was great to have so many participants this year, including 10 non-Good Delivery laboratories. The more participants we have, the more statistics we can produce. In the past, it was not easy to compare fire assay with spectroscopic results, simply because there were not enough ICP-OES analyses.

Slightly concerning, we still have relatively poor results from several ISO 17025 accredited laboratories, as well as from non-Good Delivery laboratories. We hope that the labs concerned will promptly resolve their problems.

In terms of the future of LBMA proficiency testing, we can expect the scheme to continue for a long time, with compositions of between 995 and 999.5‰ being provided.

We are hoping to see more and more improvement on the spectroscopic methods side, especially in the range of 995‰ gold, where those methods can sometimes be challenging.

An obvious extension of the LBMA proficiency testing would be on silver. The LBMA might decide to start such scheme in the future, which would be very beneficial for companies on the silver Good Delivery list.